Supporting Information

Conformational Changes of Protein upon Encapsulation of Noble Metal Clusters: An Investigation by Hydrogen/Deuterium Exchange Mass Spectrometry

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Figure S1: UV-vis spectra of Lyz and Au₈@Lyz. Protein protected clusters showed almost featureless absorption spectrum unlike monolayer protected clusters; the later exhibit distinct features that can give information about the core formed. In the case of protein protected clusters, mostly ill-defined spectra have been reported with a peak near 280 nm corresponding to absorption of the protein.



Figure S2: MALDI MS spectra of Lyz after 24 h and 48 h of hydrogen/deuterium exchange. The spectra have been fitted.



Figure S3: IR spectrum (in the amide region) of Lyz in D_2O , after heating for 2 hours at 65°C. This shows the disappearance of the band near 1550 cm⁻¹.



Figure S4: Simulated structure (simulation for 150 ns) of Lyz (A) and Au₈-Lyz (B). (B) Covalent binding of Au^{1+} ions to cysteine of Lyz.



Figure S5: Breaking of H-bonds with time for Lyz and Au₈-Lyz. This simulated data show the decrease in H-bonds in Au₈-Lyz adducts than in native Lyz, with time. Table represents the calculated secondary structure of each of the components in the case of Lyz and Au₈-Lyz.

20%



Figure S6: Time-dependent H/D exchange MS of Lyz (A), and Au_n-Lyz (B) in 20% D₂O. Inset of (A) shows the expanded view of Lyz in +10 charge state and inset of (B) shows the expanded view of in +11 charge state of Au_n-Lyz. Comparison of both spectra revealed that in 20% D₂O, the mass shift is the same for Lyz and Au_n-Lyz.



50%

Figure S7: Time-dependent H/D exchange ESI MS of Lyz (A), and Au_n-Lyz (B) in 50% D₂O.



100%

Au_n-Lyz

Lyz

Figure S8: Time-dependent H/D exchange ESI MS of Lyz (A), and Au_n-Lyz (B) in 100% D₂O.



Figure S9: (A) Overlapped image of Lyz (green) and Au₈-Lyz (purple). (B) The mapped surface area of Lyz and Au₈-Lyz.



Figure S10: ESI MS of Cu_n-Lyz adduct; inset shows the expansion of +10 charge state. Interaction of Cu^{2+} with Lyz shows that a maximum of 8 Cu can attach with Lyz. Almost similar distribution of charges like in native Lyz suggests the difference in reactivity of Au and Cu with Lyz.



Figure S11: Time-dependent H/D exchange MS of Cu_n-Lyz in 50% D₂O. The inset shows the expanded view of Cu_n-Lyz in +10 charge state. A slow exchange like in native Lyz was observed in this case.



Figure S12: Time-dependent H/D exchange ESI MS of Cu_n -Lyz in 100% D₂O. ESI MS shows that the mass shift will be different for different charge states.

XPS of the cluster



Figure S13: XPS data of $Au_8@Lyz$ cluster shows the presence of Au (0) and Au (I) in the 4f region.



Figure S14: ESI MS of alkali metal attached Lyz adducts showing similar charge state distribution to the native protein in 100% D₂O.